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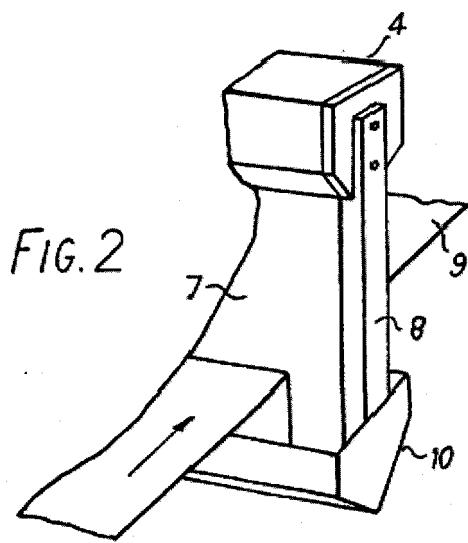
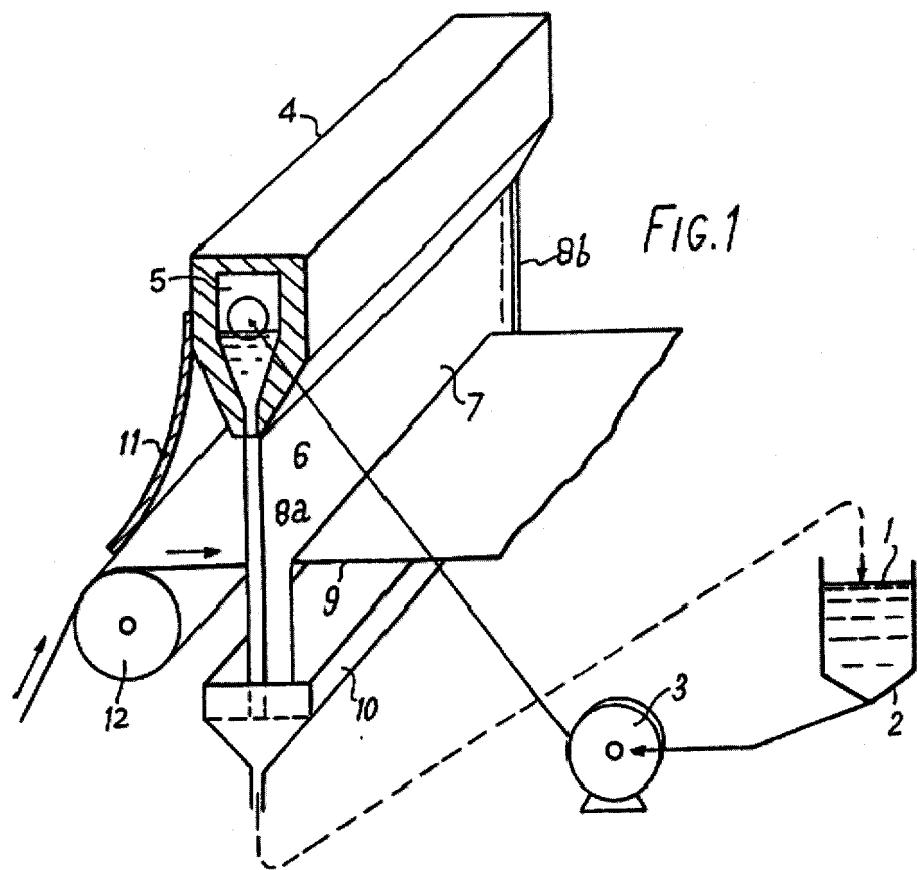
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(54) Method of producing pressure
sensitive recording sheet

(57) A pressure sensitive recording
sheet whose coated surface is in an
even state is produced by a process
employing a particular coating solution.
The solution has a static surface tension
of 42 dyne/cm or less and a surface
tension increase of 5 dyne/cm or less,
compared to its static surface tension,
when its surface is extended, and
further has a 50-mesh sieve passing
fraction of 98% or more. A curtain
coating process is used wherein the
coating solution is applied to a surface
of a continuously travelling support of
great length in the form of a
single-layer, freely falling curtain
applied at a right angle to the support.

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SPECIFICATION

Method of producing pressure sensitive recording sheet

5 This invention relates to a method of producing a pressure sensitive recording sheet using a curtain coating technique. More particularly the invention is concerned with a method of producing a pressure
 10 sensitive recording sheet by applying a coating solution for making a pressure sensitive recording layer to a surface of a continuously travelling web of support (hereinafter referred to as a "web") while the coating solution is forming a single-layer curtain
 15 which is freely falling vertically onto the web surface.
 A method of producing a pressure sensitive recording sheet using a curtain coating technique has already been disclosed in U.S. Patent No. 4,230,743. Therein, it is taught that the introduction
 20 of the curtain form to a coating process not only allows for the obtaining of thin layer coated films having excellent surface properties, but also that the pressure-density characteristics of a pressure sensitive recording sheet are also markedly improved.
 25 However, the use of such methods result in certain problems regarding the stability of a liquid film curtain.

The stabilization of a liquid film curtain made of a composition employed in the photographic art, is mentioned in published examined Japanese Patent Application No. 3544//74 (which corresponds to U.S. Patent No. 3,632,374). However, these specifications merely indicate that it is desirable to control a static surface tension of a liquid film curtain to 40 to 50
 30 dyne/cm or less and therefore, it is advantageous to add a surface active agent to the photographic composition.

However, when using coating solutions for making pressure sensitive recording sheets, such as
 40 those containing microcapsules as a main component, or those containing a color developing agent as a main component it is not possible to produce stable liquid film curtains by merely adjusting their static surface tensions to 40 to 50 dyne/cm or less.
 45 Furthermore, when the coating procedure is continued for many hours it causes such phenomenon as holes in the film curtain (hereinafter referred to as the "liquid film crawling phenomenon"). This results in the formation of a film coat having an uneven
 50 surface and may cause many uncoated areas to appear on the support surface. Even when the liquid film crawling phenomenon is not directly visible the film coat obtained frequently has an uneven surface or a lot of uncoated areas. Accordingly, the above-
 55 described coating process suffers a fatal disadvantage from the viewpoint of security of producing film coats having even surfaces in making pressure sensitive recording sheets. Therefore, further improvements in this regard have been required.
 60 An object of this invention is to provide a method for producing a pressure sensitive recording sheet which has a uniform coated surface.

This object is attained effectively by the use of a coating solution wherein static surface tension is controlled to 42 dyne/cm or less, surface tension increase is 5 dyne/cm or less when its surface is extended, compared to its static surface tension, and further wherein a proportion of 98% or more of the coating solution can pass through a 50-mesh sieve.

65 70 Within the disclosed process a coating solution for producing a pressure sensitive recording sheet is applied to a surface of continuously travelling web while the coating solution forms a single layer, freely falling, vertical curtain.

75 The invention will be further described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a diagrammatic perspective view illustrating a coating apparatus employed in an embodiment of this invention; and

80 Figure 2 is an enlarged fragmentary perspective view of the most important part of the coating apparatus, wherein 4 is a solution supplying head, 6 is a slit, 7 is a freely falling vertical curtain, both 8
 85 and 9 are guiding rods, 9 is web, 10 is a solution receiving tank, and 11 is a wind blocking plate.

In this invention, static surface tension is determined using a Cahn's tensiometer for measuring a dynamic surface tension on the basis of the principle
 90 of the vertical sheet process (Wilhelmy's process).

An increase in surface tension due to surface extension, compared to the static surface tension, is determined by reading off the maximum surface tension in the recorder while making the solution surface periodically repeat alternate motions of extension and compression. The frequency of motion is 13.5 rpm, the minimum surface area is 9
 95 cm², and the maximum surface area is 45 cm². Increase in surface tension due to surface extension

100 is then determined by finding the difference between the value read off and the static surface tension. The principle of measurement using Cahn's dynamic tensiometer and related matters are described in detail in *J. Colloid Interface Sci.*, volume 39, pages
 105 323 - 330 (1972).

The above-described object of this invention is attained only when all of three essential conditions described above are satisfied. It is not possible to obtain the object of this invention even if only one
 110 essential condition is not satisfied.

If the increase in surface tension due to the surface extension exceeds 5 dyne/cm, compared to the static surface tension (even if the static surface tension is less than 42 dyne/cm), the liquid film crawling
 115 phenomenon occurs frequently in the curtain.

Accordingly, it is only possible to obtain a coated sheet having elliptical, very large uncoated areas. Furthermore, if the 50-mesh sieve passing fraction of a coating solution is less than 98% (even though its
 120 static surface tension is controlled to 42 dyne/cm or less, and further, even if an increase in its surface tension due to the surface extension is controlled to 5 dyne/cm or less, compared to its static surface tension), it is only possible to obtain a coated sheet

having a number of small elliptical uncoated areas or scattered uncoated spots. However, the liquid film crawling phenomenon is not observed in the curtain.

The expression "a coating solution containing

5 microcapsules as a main component" in this invention is intended to include a solution and a dispersion in which microcapsules are dissolved and dispersed, respectively, in water together with a binder and a protective agent. The concentration of the mixture of microcapsules, binder and protective agent, range from 10 wt% to 60 wt%, which have viscosities adjusted to 20 cp to 500 cp. The mixture of the binder and the protective agent is generally compounded in amounts of 5 parts by weight or larger, preferably 10 to 70 parts by weight, and more preferably 30 to 60 parts by weight, with 100 parts by weight of microcapsule. The protective agent is usually compounded in an amount of 50 to 400 parts by weight with 100 parts by weight of binder.

20 In this invention, the term microcapsule refers to a fine capsule which is constructed so that its contents consist of an oily solution of a basic, colorless color-forming agent. A capsule wall covers the contents and is constituted with a macromolecular substance

25 insoluble to both water and the oily solution. The capsule has an average diameter of 1 to 20 μ . Specific examples of capsule wall material include the combinations of polycations and polyanions, such as gelatin-gum arabic and the like; and combinations of polycondensed compositions, such as polyisocyanate-polyamine, polyisocyanate-polyurea-formaldehyde, melamine-formaldehyde, and so on.

30 Examples of methods of producing such microcapsules include: phase separation methods using an aqueous solution (U.S. Patents 2,800,457, 2,830,458, 3,687,365 and 3,897,361; the external polymerization process (U.S. Patents 3,980,156, 4,031,140, 4,105,323, 4,100,103, 4,089,802 and 40 4,037,376; British Patent 1,355,124; published examined Japanese Patent Application No. 12518/63; and Japanese Patent Application No. 126958/79); the International polymerization process (published examined Japanese Patent Application Nos. 19674/63, 2882/67, 2883/67, 8669/67, 9654/67 and 11344/67; British Patents 1,031,076, 1,091,077, 950,443 and 1,046,409); methods of polymerizing capsule wall materials in oil droplets (British Patents 2,968,300 and 3,791,889), and the 50 molten dispersion quenching process (British Patents 952,007 and 965,074; and so on).

This color-forming agents which can be used in this invention have such a property as to form a color by donating an electron or by accepting a proton of an acid or the like.

55 It includes compounds which are nearly colorless usually but are not restricted particularly to colorless ones. Examples of useful color forming agents include those having a skeleton moiety which

60 undergoes ring opening or cleavage upon contact with a color developing agent; for example, lactone, lactam, sulfone, spiropyran, ester, amide or so on. Specific of other color-forming agents, include Crystal Violet Lactone, Benzoyl Leucc Methyleine Blue, Malachite Green Lactone, Rhodamine B lac-

tam, and 1,3,3 - trimethyl - 6' - ethyl - 8' - butoxyindolinobenzospiropyran.

These color-forming agents are dissolved in particular solvents and encapsulated.

70 Useful solvents include natural or synthetic oils which may be used independently or in their combination. Specific examples of the solvent include cotton seed oil, kerosene, paraffin, naphthene oil, alkylated biphenyl, alkylated terphenyl, chlorinated paraffin, alkylated naphthalene and diarylethane. Methods for encapsulating these solutions are set forth above.

Binders useful in this invention, include latexes such as styrene-butadiene rubber latex, styrene-
80 butadiene-acrylonitrile latex, styrene-butadienemaleic anhydride copolymer latex; water soluble natural high polymers such as proteins (e.g., gelatin, gum arabic, albumin, casein); celluloses (e.g., carboxymethyl cellulose, hydroxyethyl cellulose); and
85 charoses (e.g., agar, sodium alginate, starch, carboxymethyl starch, starch phosphate); water soluble synthetic high polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid, polyacrylamide, isobutylene-maleic anhydride copolymer,
90 ethylene-maleic anhydride copolymer and polyvinylbenzene sulfonate. Preferred high polymers are those have molecular weights of about 1,000 to 10,000,000 and in particular, 10,000 to 5,000,000.

Preferred protective agents used in this invention
95 are granular substances which exist in a solid state at ordinary temperatures. Specific examples thereof include starch grains (as described in British Patent 1,232,347), fine powders of polymers (as described in U.S. Patent 3,625,736), microcapsules not containing color-forming agents (as described in British Patent 1,235,991), inorganic grains such as talc, kaolin, bentonite, agalmatolite, zinc oxide, titanium oxide and aluminum. The preferred mean diameter of these grains (measured by a volume average method) is 3 to 50 microns and a particularly preferred range is 5 to 40 microns. Further, these grains function more effectively when they are larger than the microcapsules containing color-forming agents.

Fibrous materials such as cellulose fine powder
100 and the like may be used as the protective agent. However, when using such powder it is necessary to restrict the compounding ratio of the powder to the total amount of microcapsule, binder and protective agent to 0 to 5%. Therefore, granular substances are
105 preferable over fibrous ones.

The color developing agent of this invention is intended to include absorbable or reactive compounds which have electron accepting or proton donating abilities and develops colors on contact with
110 the above-described color-forming agents. Examples of useful color developing agents include acid clay, bentonite, clay minerals such as kaolin and so on, phenol-formaline novolak, metal processed novolak and zinc salts of aromatic carboxylic acids.
115 The above-described color developing agents may be used in combination.

The term "coating solution containing a color developing agent as a main component" refers to a solution or a dispersion wherein a color developing
120 agent is dissolved or dispersed respectively in water

or a different solvent together with a binder. The total concentration of the solid component therein is usually adjusted to about 10 to 60 wt%. The viscosity of the solution is adjusted to 20 to 500 cps.

5 Examples of binders for the color developing agent include acrylate series latexes, vinyl acetate series latexes and styrene-butadiene series latexes. In particular, styrene-butadiene latex having a polymerization degree of 500 to 100,000 is preferably 10 and used in an amount of 5 parts by weight or larger and more preferably, 10 to 30 parts by weight per 100 parts by weight of the color developing agent. In addition, when a latex binder is used, other water soluble binders can be used in combination with it, 15 and such a combined use can improve the results obtained such as the applied film strength and dispersibility of the color developing agent.

Specific examples of water soluble binders which may be employed in the combination include water 20 soluble natural high polymers such as: proteins (e.g., gelatin, albumin, casein); celluloses (e.g., carboxymethylcellulose, hydroxymethyl cellulose); saccharoses (e.g., agar, sodium alginate, carboxymethyl starch, gum arabic); and water soluble 25 synthetic high polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid, polyacrylamide, polyvinylbenzenesulfonic acid, and other latexes.

When these binders are combined, the total 30 amount used is preferably 20 parts by weight or less per 100 parts by weight of color developing agent, and the sum total of the binders of latex system and these water soluble binders is preferably 40 parts by weight or less. When the sum total exceeds 40 parts 35 by weight, the color developability is lowered and the production cost increases.

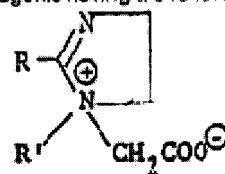
By adding surface active agents to a coating solution containing microcapsules as a main component, or a coating solution containing a color developing 40 agent as a main component which are prepared in the static surface tension of the coating solution and the increase the surface tension of the coating solution due to its surface extension, compared to its 45 static surface tension, to not greater than 42 dyne/cm and not greater than 5 dyne/cm, more preferably not greater than 38 dyne/cm and 4 dyne/cm, and the most preferably not greater than 35 dyne/cm and 3 dyne/cm, respectively.

50 Surface active agents which may be used in this invention include: anionic surface active agents of carboxylic acid salt, sulfonic acid salt, sulfuric acid ester, phosphoric acid ester; cationic surface active agents of quaternary ammonium salt, amine salt, 55 pyridinium salt, benzyl halide; amphoteric surface active agents of betaine, sulfobetaine, imidazoline; and nonionic surface active agents of polyethylene glycol, polyhydric alcohol-fatty acid ester.

These agents may be added independently or in 60 combination.

Specific examples of surface active agents which are particularly favorable in this invention include sodium alkylsulfosuccinates, sodium alkylbenzenesulfonates, alkylbenzenesulfonic acid-65 triethanolamine salts, phosphoric acid esters of

alkylalcohol-oxidized ethylene adducts, alkyl-dimethylbenzylammonium chloride, alkyl-dimethylbetaines, alkylimidazoline type amphoteric surface active agents having the following general formula:



wherein R is alkyl group having 1 to 20 carbon atoms and R' is alkyl group having 1 to 20 carbon atoms.

A coating solution for a pressure sensitive recording sheet which is prepared in the above-described manner is filtered through a 50-mesh sieve, more preferably a 100-mesh sieve, and most preferably a 200-mesh sieve, and then sent to a curtain coating head.

The thus obtained coating solution for the pressure sensitive recording sheet of this invention is very useful for forming a stable, single-layer, freely falling, vertical curtain free of the liquid film crawling phenomenon. Furthermore, such a coating solution is useful for providing a uniform surface of coat 50 when applied to continuously travelling web using the curtain coating technique.

Particular embodiments of the film applying apparatus of the present invention are described below. However, it is to be understood that this invention is not limited to the particular arrangement of parts shown as such devices may, of course, vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting 100 since the scope of the present invention will be limited only by the appended claims.

Figure 1 is a schematic diagram of a coating apparatus for producing a pressure sensitive recording sheet which illustrates one of embodiments of this invention. Figure 2 is a detailed diagram of the

105 A previously prepared coating solution 1 which contains as a main component microcapsules or a color developing agent is sent to a solution supplying head 4 from a tank 2, in which the coating solution is stored, by means of a quantitative pump 3. A certain amount of a coating solution and a coated amount of the final product bear a linear relationship to each other. Therefore, the amount of the solution 110 sent to the solution supplying head must be controlled with high accuracy. Accordingly, a variable type non-pulsating current, constant flow rate pump is suitable as the quantitative pump 3.

The solution supplying head 4 has a pocket 5 115 within, and a slit 6 of high precision at the lower part. At the inside of the pocket 5 is being filled with the supplied coating solution 1, the dynamic pressure applied to the coating solution upon the supply thereof is allowed to die away. When a dynamic 120 equilibrium state is reached, a quantity of the current of the coating solution 1 flowing into the pocket 5 is balanced with a quantity of the current flowing out of the slit 6 and the height of the solution surface inside the pocket 5 is maintained constant. Consequently, 125 the coating solution flowing out of the slit 6 under 130

the influence of gravity falls in such a state that the current of the coating solution is uniform in its cross direction, and forms a freely falling vertical curtain 7. Thereupon, guiding rods 8a and 8b are provided as if they were supporting both sides of the curtain 7 in order to enhance the stability of the curtain 7 as a liquid film. An appropriate width of the slit 8 ranges from 0.1 mm to 1.0 mm, preferably from 0.2 mm to 0.6 mm, and particularly preferably from 0.2 mm to 10 0.4 mm.

The freely falling curtain 7 of the coating solution 1 collides with a continuously travelling web 9, and is coated on the web 9. Then, the guiding rods 8a and 8b are arranged at an interval beyond the width of 15 the web 9 and so, the freely falling vertical curtain 7 is formed with a width wider than that of the web 9. A portion of the coating solution 1 which falls down protruding beyond the width of the web 9 is collected by a solution receiving tank 10, and recycled 20 into the coating solution tank 2. The reason why the curtain 7 is formed with a width wider than that of the web 9 is to prevent a thick coating at the vicinity of both side ends of the coating layer, which usually occurs if the width of the curtain 7 is shorter than 25 that of web 9. In addition, on the side of the upper course of the travelling web 9, starting from the position where the freely falling curtain 7 collides with the web 9 (hereinafter the "coating part"), an air shielding plate 11 is provided. The plate intercepts 30 an air flow which accompanies the travelling web 9. Through this careful consideration the freely falling curtain can reach the web 9 without being disturbed. Further, the first travelling direction of the web 9 is turned to another direction by means of a roller 12 just upstream of the coating part such that the curtain is not disturbed by air formed by the travelling web 9. The turning angle is determined in a manner 35 so as to minimize influences of the attending air flow upon the coating part. Moreover, this film applying apparatus is designed so that when the coating procedure is interrupted by the cutting of the web or so or the coating solution 1 may be also collected in the 40 solution receiving tank 10.

In this invention, a moderate travelling speed of 45 the web ranges from 350 m/min to 2,000 m/min, and an appropriate flow rate of the liquid film curtain ranges from 1 to 3 g/sec/cm.

Specific examples of webs employable in this invention include commonly high-grade paper, mid-grade paper, regenerated paper, machine-coat paper, art paper, cast-coat paper, synthetic paper, resin-coated paper and plastic films.

An adequate dry coverage of the coating solution containing microcapsules as a main component is 3 55 g/m² or above, and preferably from 4 to 6 g/m². However, an adequate dry coverage of a coating solution containing a color developing agent as a main component depends upon what kind of color developing agent is contained in the coating solution. In the case 60 of clays, it is 4 g/m² or above, and preferably ranges from 5 to 8 g/m². In the cases of phenol resins and metal salts of aromatic carboxylic acids, they are 0.5 g/m² or above, and preferably range from 0.8 to 5 g/m².

65 In addition, a proper height of the freely falling

vertical curtain of this invention, though it should be determined depending upon the solution supplying amount, is usually 40 cm or less, preferably 30 cm or less, and more particularly within the range of 10 to 70 20 cm.

When producing a pressure sensitive recording sheet which has a coated layer containing microcapsules as a main component on one side of a support and a coated layer containing a color developing 75 agent as a main component on the other side of the support, it is desirable to form the respective layers to be coated on each side of the support in accordance with the curtain coating process illustrated in this invention. However, it is permissible to form 80 either of the layers using the curtain coating process of this invention and to form the other layer using the air knife coating process or the blade coating process.

The present invention will now be illustrated in 85 greater detail by reference to the following examples.

In the following examples, "parts" and "%'" are by weight, and "amounts coated" are on dry basis.

EXAMPLE 1

90 Five parts of pigskin acid-processed gelatin and five parts of gum arabic were dissolved in 40 parts of 40°C water, and thereto was added 0.28 parts of Turkey red oil as an emulsifier. Then, 55 parts of disopropiophenone having dissolved therein 2.5% of 95 Crystal Violet Laccone (hereinafter CVL) and 2% of benzoyl leuco Methylene Blue (hereinafter BLMB) was added to the above-described colloidal solution under vigorous stirring for emulsification to form an emulsion. The stirring was discontinued when 100 the average size of oil droplets became 7.5 μ. Thereto, 170 parts of 40°C water was added. Thereafter, 20% acetic acid was added dropwise thereto, while continuing the stirring, till the emulsion was adjusted to pH = 4.6. Then, the emulsion was cooled 105 to 10°C while continuing the stirring. While maintaining the system at 10°C, 0.8 parts of 50% aqueous solution of glutaraldehyde and 0.2 parts of 37% aqueous solution of formaldehyde were added. To the system was added 27 parts of 7% aqueous solution of sodium salt of carboxymethyl cellulose, and thereto was further added dropwise 10% aqueous 110 solution of sodium hydroxide in order to adjust the pH value of the system to 10. Thereafter, the temperature of the system was raised to 45°C while continuing the stirring, and thereto were added 100 parts of 115 13% aqueous solution of polyvinyl alcohol (whose saponification degree and polymerization degree were 98% and 500, respectively), 24 parts of starch grains (having an average diameter of 15 μ) and 5 120 parts of talc.

To the resulting dispersion 26 parts of 2% aqueous solution of sodium alginate and, as a surface active agent, 2.8 parts of 37% aqueous solution of lauryldimethylbetaine were added. By the addition of 125 water a total concentration of solid components was controlled to 20%. Thereafter, the dispersion was filtered through a 200-mesh sieve. A coating solution containing microcapsules as a main component was obtained.

130 This coating solution has a viscosity of 52 cp at

25°C and a static surface tension of 33.3 dyne/cm, and showed a surface tension increase of 2.3 dyne/cm, compared to its static surface tension, by the surface extension.

5 COMPARISON 1

A coating solution was prepared in the same manner as in Example 1 except that it was not filtered through the 200-mesh sieve.

10 A 50-mesh sieve passing fraction of this coating solution was 95%.

COMPARISON 2

A coating solution was prepared in the same manner as in Example 1 except that 0.3 parts of Turkey red oil (50% aqueous solution) was used as a surface active agent instead of lauryldimethylbetalaine.

This coating solution had a viscosity of 52 cp at 25°C and a static surface tension of 43.2 dyne/cm, and showed a surface tension increase of 4.0 dyne/cm, compared to its static surface tension, by 20 surface extension.

COMPARISON 3

A coating solution was prepared in the same manner as in Example 1 except that 0.9 parts of 5% aqueous solution of perfluorooctylcarboxylic acid was 25 used as a surface active agent instead of lauryl-

dimethylbetalaine.

This coating solution had a viscosity of 52 cp at 25°C and a static surface tension of 21.5 dyne/cm, and showed a surface tension increase of 6.7 dyne/cm, compared to its static surface tension, by the surface extension.

Each of the coating solutions prepared in the above-described Example 1 and Comparisons 1 to 3 was coated on a web made of thin paper which had a weighed quantity of 40 g per square meter and a width of 1,600 mm. The paper was coated while it continued travelling at 500 m/min while being supplied to the solution supplying head in a supplying amount of 10.2 kg per one minute. The supply head formed a freely falling vertical curtain having a height of 10 cm using an extrusion coating apparatus as illustrated in Figures 1 and 2 which had a slit having a length of 1700 mm and a width of 0.4 mm. The thus coated solution was, then, subjected 40 to a drying processing.

A measurement was taken of the number of the liquid film crawling phenomenon occurred in the coating procedure. Furthermore, the condition of the surface of each of the coated papers were compared.

50 The results obtained are shown in Table 1.

Table 1

	Liquid Film Crawling of Curtain	Surface State of Coated Paper
Example 1	0 time/hr.	Uniform surface of coat having coated amount of 14.5 g/m ² .
Comparison 10 time/hr.		Presence of elliptical uncoated areas (measuring 1 to 5 mm in length and 0.3 to 2 mm in breadth), which number is 40 per square meter
Comparison 275 times/hr.		Frequent uncoated areas (measuring 50 mm or larger in length and 20 mm or larger in breadth) due to frequent liquid film crawling phenomena
Comparison 349 times/hr		The same as Comparison 2
In Example 1, differing from Comparisons 1 to 3, the stable curtain free of the liquid film crawling phenomenon was formed. Furthermore, the surface of the coated layer was in an even state with no uncoated areas. It can be seen from these results that this invention gives greatly improved results.		tively, and 2 parts of sodium salt carboxymethyl cellulose with vigorous stirring to produce oil droplets 75 having an average diameter of 5.3 μ . Thereafter, the temperature of the system was gradually raised to 90°C in order to complete the encapsulating reaction. To this solution, 12 parts of styrene-butadiene latex (48% aqueous solution) and 12 parts of starch grains 80 (having an average size of 20 μ) were added. Subsequently, 0.6 parts of 30% aqueous solution of dodecylbenzenesulfonic acid triethanolamine salt was added to the mixture as a surface active agent, and further water was added to make a total concentration of solid components in this mixture adjust to 37%. Thereafter, the resulting solution was filtered 85 through a 50-mesh sieve. Thus, a coating solution containing microcapsules as a main component was obtained.
EXAMPLE 2		90 This coating solution had a viscosity of 74 cp at 25°C and a static surface tension of 37.2 dyne/cm, and showed a surface tension increase of 3.5 dyne/cm, compared to its static surface tension, by the surface extension.
CVL and BLMB were added as color forming agents in concentrations of 2.5% and 2% respectively to 60 parts of diisopropylnaphthalene, and dissolved therein by heating at a temperature of 95°C.		
This oily solution was cooled to 20°C, 5 parts of the addition product including 3 mole of tolylene diisocyanate and 1 mole of trimethylolpropane as 65 the first wall film forming substance and 1 part of the addition product of sorbitol and propylene oxide as the second wall film forming substance were added to and dissolved in the cooled oily solution. The resulting oily solution was added to 120 parts of 18°C aqueous solution dissolving therein 4 parts of polyvinyl alcohol (whose saponification degree and polymerization degree were 88% and 500, respec-		

Using an extrusion coating apparatus as illustrated in Figures 1 and 2 which had a slit having a length of 860 mm and a width of 0.3 mm, the thus obtained coating solution was coated on a web. The web made of thin paper which had a weighed quantity of 50 g per square meter and a breadth of 800 mm and continued travelling with a speed of 1000 mm/min while the solution was being supplied to the solution supplying head in a supplying amount of 9.3 kg per one minute. The supplied solution kept forming a freely falling vertical curtain having a height of 15 cm. The thus coated solution was, then, subjected to a drying processing.

At the time of coating, the liquid film crawling phenomenon was observed once per 60 minutes in the liquid film curtain. However, such a frequency of occurrence of the phenomenon is insignificant value from the viewpoint of practical use. In addition, the paper had a coated layer with a uniform coated amount of 4.0 g/m², and the surface of the coated layer was in an even state.

EXAMPLE 3

100 Parts of diisopropynaphthalene having dissolved therein 2.5% of CVL and 2% of BLMB was added to 100 parts of 4.4% aqueous solution of partial sodium salt of polyvinylbenzenesulfonic acid (having an average molecular weight of 500,000), which is adjusted to pH = 4, for emulsified dispersion to form an o/w emulsion whose oil droplets had an average size of 4.5 μ . Separately, 6 parts of melamine, 11 parts of 37% aqueous solution of formaldehyde and 83 parts of water were mixed with stirring as they were heated at a temperature of 60°C. After 30 minutes of stirring and heating, a transparent aqueous solution of the mixture of melamine, formaldehyde and an initial condensation product of melamine and formaldehyde was obtained. This aqueous mixed solution was admixed to the above-described emulsion and thereto, 20% aqueous solution of acetic acid was added dropwise with stirring to adjust a pH value of the system to 6.0. Then, the temperature of the solution was raised to 66°C and kept at the same temperature for 30 minutes to result in completion of the encapsulating reaction.

To this solution were added 200 parts of 20% aqueous solution of etherified starch, 47 parts of starch grains (having an average size of 40 μ) and 10 parts of talc.

Thereinto, 32 parts of 2% aqueous solution of 50 sodium dioctylsulfosuccinate was added as a surface active agent and further, water was added to make a total concentration of solid component in the solution adjust to 32%. Thereafter, the thus obtained solution was filtered through a 100-mesh sieve.

Thus, a coating solution containing microcapsules as a main component was prepared.

This coating solution had a viscosity of 98 cp at 25°C and a static surface tension of 28.1 dyne/cm, and showed a surface tension increase of 0.7 dyne/cm, compared to its static surface tension, by the surface extension.

Using an extrusion coating apparatus as illustrated in Figures 1 and 2 which had a slit having a length of 860 mm and a breadth of 0.4 mm, the thus prepared coating solution was coated on a web. The

web was made of thin paper which had a weighed quantity of 40 g/m² and a breadth of 800 mm and continued travelling with a speed of 700 mm/min while the solution was being supplied to the solution supplying head in a supplying amount of 9.4 kg per one minute. The supplied solution kept forming a freely falling vertical curtain having a height of 13 cm. The thus coated solution was, then, subjected to drying processing.

The liquid film crawling phenomenon of a curtain at the time of coating did not occur at all in this case, and the coated amount of the coated paper obtained was 5.0 g/m² and its surface formed in an even state.

EXAMPLE 4 to 6

300 Parts of water and 0.5 parts of sodium hexametaphosphate were placed in a tank equipped with a Kedzie's mill, and dissolved therein with agitating. Next, 5 parts of 50% aqueous solution of sodium hydroxide was added thereto while continuing the agitation. In addition 86 parts of 48% aqueous solution of styrene-butadiene latex was added thereto. Into the thus prepared aqueous solution was added and dispersed 142 parts of acid-processed activated clay while continuing the agitation. Subsequently 20 parts of kaolin and 3.5 parts of magnesium oxide were added and dispersed therewith. The agitation was continued for 20 minutes leaving the mixed system as it was. Furthermore, 16 parts of 30% aqueous solution of starch phosphate was added thereto. Subsequently, the pH value of the resulting system was adjusted to 9.9 by the addition of 25% aqueous solution of sodium hydroxide.

Next, 6 parts of 30% aqueous solution of dodecylbenzenesulfonic acid triethanolamine salt was added as a surface active agent to the system. In addition a total concentration of solid components in the system was controlled to 30% by adding water thereto. Thus, a coating solution containing color developing agents as a main component was obtained.

This coating solution had a viscosity of 62 cp at 25°C and a static surface tension of 31.6 dyne/cm, and showed a surface tension increase of 1.7 dyne/cm, compared to its static surface tension, by the surface extension.

A portion of this coating solution was filtered through a 50 mesh sieve (Example 4), another portion through a 100-mesh sieve (Example 5), and still another portion through a 200-mesh sieve (Example 115). The residual portion of this coating solution was not filtered through any sieves (Comparison 4). Therein, a 50-mesh sieve passing fraction of the residual portion was 94%.

Using an extrusion coating apparatus as illustrated in Figures 1 and 2 which had a slit having a length of 1700 mm and a breadth of 0.4 mm, each of the thus obtained portions of the coating solution was coated on a web. The web was made of thin paper which had a weighed quantity of 40 g per square meter and a breadth of 1600 mm and continued travelling with a speed of 700 mm/min while the solution was being supplied to the solution supplying head in a supplying amount of 21.8 kg/min. The supplied solution formed a freely falling vertical curtain having a height of 12 cm. The coated solution

was then dried.

The liquid film crawling phenomenon at the time of coating was not observed at all in the curtain made of the coating solution prepared in each of Examples 4 to 6 and Comparison 4. Furthermore, all of these curtains were stable. However, the coated papers obtained differed in their surface states from one another, as described in Table 2.

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	<i>Table 2</i>	<i>Surface State of Coated Paper (Number of Occurrence of Scattered Coated Spots Having Size of 1 mm or Smaller)</i>
Example 4	5 per square meter	
Example 5	1 per square meter	
Example 6	0 per square meter	
Comparison 4	175 per square meter	

The coated papers of Example 4 to 6 had much less uncoated areas than the coated paper of Comparison 4, and showed nearly or completely uniform surface states. Accordingly, it can be seen that this invention can exhibit remarkable effects upon the surface property of coated paper.

EXAMPLE 7

Using a Kedzie's mill 10 parts of zinc 3,5 - di - α -methylbenzylsalicylate, 10 parts of zinc oxide, 60 parts of acid clay, 1 part of styrene oligomer and 40 parts of aluminium oxide were dispersed into 170 parts of water containing therein 1 part of sodium hexametaphosphate. This dispersion was processed using a sand grinder by 100 liter per hour. To the dispersion obtained were added 50 parts of 10% aqueous solution of polyvinyl alcohol (having a saponification degree of 98% and a polymerization degree of 1700) and 20 parts of styrene-butadiene latex (48% aqueous solution).

Subsequently, 10 parts of 20% aqueous solution of phosphoric acid ester of the addition product of 1 mole of tridecyl alcohol and 6 mole of ethylene oxide was added thereto as a surface active agent. Furthermore, water was added to make a total concentration of solid components of 34%. Thus, a coating solution containing color developing agents as a main component was obtained.

This coating solution had a 200-mesh sieve passing fraction of 98% or more, a viscosity of 75 cp at 25°C and a static surface tension of 32.8 dyne/cm, and showed a surface tension increase of 3.4 dyne/cm, compared to its static surface tension, upon the surface extension.

Using an extrusion coating apparatus as illustrated in Figure 1 and 2 which had a slit having a length of 860 mm and a breadth of 0.4 mm, the thus prepared coating solution was coated on a web. The web was made of thin paper which had a weighed quantity of 50 g/m² and a breadth of 800 mm. The web travelled at a speed of 600 m/min while the solution was being supplied to the solution supplying head in a supplying amount of 6.8 kg/min. The supplied solution formed a freely falling vertical curtain having a height of 10 cm. The thus coated solu-

tion was, then, subjected to a drying processing.

The liquid film crawling phenomenon at the time of coating was not observed at all in the curtain made of this coating solution. The coated amount of 70 the coated paper obtained was 4.5 g/m² and its surface was in an even state.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS:

1. A method of producing a pressure sensitive recording sheet comprising the steps of:
 - 80 preparing a coating solution containing microcapsules or a color developing agent as a main component, said coating solution being controlled to have a static surface tension of 42 dyne/cm or less, and when its surface is extended having a surface tension increase of 5 dyne/cm or less as compared to its static surface tension, and further having a 50-mesh sieve passing fraction of 98% or more;
 - allowing said solution to form a free-falling, single-layer, vertical curtain, and
 - 90 applying said curtain film to a surface of a web travelling continuously across said free-falling vertical curtain.
2. A method for producing a pressure-sensitive recording sheet as claimed in Claim 1 wherein said coating solution contains one or more surface active agents.
3. A method for producing a pressure-sensitive recording sheet as claimed in Claim 1 wherein said static surface tension is controlled 38 dyne/cm or 100 less.
4. A method for producing a pressure-sensitive recording sheet as claimed in Claim 1 wherein said surface tension increase is controlled 4 dyne/cm or less.
- 105 5. A method for producing a pressure-sensitive recording sheet as claimed in Claim 1 wherein said coating solution is controlled to have a 100-mesh sieve passing fraction of 98% or more.
6. A method as claimed in Claim 1, substantially 110 as described herein.
7. The features as herein described, or their equivalents, in any novel selection.

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